California Environmental Protection Agency

Air Resources Board

Engineering and Laboratory Branch
Monitoring and Laboratory Division

MLD SOP ES04

STANDARD OPERATING PROCEDURE FOR WATER DETERMINATION IN CONSUMER PRODUCTS USING GAS CHROMATOGRAPHY

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1 INTRODUCTION

This procedure is used for the measurement of water in consumer products and is based on U.S. EPA Method 24/24A, Part 60, Title 40, CFR, Appendix A and ASTM D3792-86. Product samples are diluted with solvent and analyzed by gas chromatography. This procedure is useful for quantitating product samples containing concentrations of 50-100% water. Any mention of brand names or commercial products are included as examples only, and any equivalent products can be used.

2 SUMMARY OF METHOD

The samples of consumer products are prepared as a 1:10 u/v dilution in 1-methoxy-2-propanol (MPA). After thorough mixing, the solution may require centrifuging to remove insoluble material. If under special circumstances another solvent is required, then all standards, controls and matrix spikes are to be made with the same solvent and analyzed with those samples.

The diluted sample is then analyzed by gas chromatography/thermal conductivity detector to determine the water concentration in the sample. The data is reported in weight fraction of water in the product.

3 INTERFERENCES/LIMITATIONS

Compounds with similar retention times to water can interfere with this procedure. These can include dissolved aerosol propellant components.

4 APPARATUS

4.1 Glass vials with Teflon-lined caps to contain prepared samples and standards. Ten ml vials with minimal headspace are desirable.

4.2 Gas Chromatograph (GC) configured with Thermal Conductivity Detector (TCD).

4.3 Stainless steel column, 6' X 1/8" o.d., packed with HayeSep C, 80/100 mesh, or any analytical column capable of separating water from all possible interferences and showing a sharp, clean peak that will allow the analyst to achieve a desired detection limit.

4.4 Ten ml volumetric glassware. The volumetric flasks are used to dilute the sample 1:10 wt./volume and for making working standards.

4.5 Analytical balance capable of weighing to the nearest 0.001 gram.

4.6 Volumetric pipettes with bulb or automated pipetters capable of measuring out 1 to 5 mls.

4.7 Small disposable glass pipettes with bulbs.

5 REAGENTS

5.1 1-Methoxy-2-propanol (MPA), anhydrous, stored by adding approximately 10 grams of molecular sieve 4A per liter.

5.2 Water: ASTM Type I

5.3 Calibration standards: Five calibration standards are prepared by adding 0.200, 0.400, 0.600, 0.800 and 1.00 gm ASTM type I water to 1-methoxy-2-propanol (MPA) in 10.0 ml volumetric flasks. Dilute to the mark with MPA.

6 GASES

6.1 Helium: Grade 5.

7 SAMPLE PREPARATION PROCEDURE

7.1 Properly label glassware and vials with correct Lab ID number.

7.2 Mix product sample well.

7.3 Using a volumetric pipette, add one ml of sample into the tared 10 ml flask, and record sample weight.

7.5 Dilute to the mark with MPA. This delivers approximately a 1:10 dilution factor.

7.6 Mix contents well.

7.7 Sample is ready for injection into the GC. Injection volume is one microliter (1 μL).

8 ANALYSIS

8.1 The normal analytical sequence is the analysis of a blank solvent sample, followed by the calibration standards, a Control Sample, then analyses of the diluted samples and duplicates. Control Samples should be analyzed every tenth sample, and the results recorded on the procedure Control Chart.

8.2 Column should be conditioned to manufacturer's recommendations.

8.3 The GC should be able to separate water from other compound peaks and the chromatograph should show a sharp, clean distinguishable water peak that will allow the chemist to achieve a target detection limit.

9 GAS CHROMATOGRAPHY PARAMETERS

9.1 Column: 6' x 1/8" packed stainless steel column with Hayesep C 80/100 mesh.

9.2 GC model: HP 5890 Plus.

9.3 Acquisition/Integration: HP Chemstation hardware/software package.

9.4 Oven program:

Initial Temperature	80°C
Initial Time	1.20 min
Rate (°C/min)	20.0
Final Temperature (°C)	210
Final Time (min)	6.20

9.5 Injection port temp: 250 °C.

9.6 TCD detector temp: 250 °C.

9.7 TCD sensitivity: Low.

9.8 TCD polarity: +

9.9 Peak width: 0.053 min.

9.10 Data rate: 5.000 Hz.

9.11 Column flow rate: 30 cc/min.

9.12 TCD reference flow rate: 45 cc/min.

9.13 Oven equilibration time: 0.30 min.

10 QUALITY CONTROL

10.1 A MPA solvent blank must be analyzed for each batch of samples. The water concentration in the solvent blank must be less than 0.1% wt./volume.

10.2 A Control Sample corresponding to 25% wt./vol. water is analyzed after the calibration standards to check for accuracy. (Distilled water must be accurately weighed on an analytical balance and diluted to volume in the same manner as the samples to achieve the desired concentration level). The result must be recorded on the procedure Control Chart and must fall within the control limits of ±3s. The control sample must be analyzed for every 10 samples to check for drift.

10.3 The calibration curve resulting from the analysis of the 5 calibration standards must have a correlation coefficient of greater than 0.98.

10.4 The LOD for the water analysis should be determined annually. The LOD for this method is 1.0 mg/ml.

11 CALCULATIONS

The weight fraction of water in the non-aerosol product is calculated as follows:

$$\text{Weight Fraction Water} = \{H_2O \text{ (mg/ml)} / \text{sample weight (g)}\} \times 10^{-2}$$

12 REFERENCES

12.1 ASTM Method D3792-86, "Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph" (EPA Method 24).

12.2 "Determination of Volatile Organic Compounds (VOC) in Water Based Aerosol Paints". Bay Area Air Quality Management District Method 36, August 31, 1990.

Appendix A

GC WATER PROCEDURE: OPERATION OF THE 5890

1. GC/Water analysis is run on the HP 5890, using injector A (front) and detector A (the TCD). Operation is on the same instrument that the Acetone/Alcohol procedure is run (on injector B, back and detector B, FID). Each procedure runs independently of the other, using separate injector towers.

2. Preparation of Calibration Standards:
   To 10 mL volumetric flask, weigh ASTM Type 1 (from the Nanopure system in the back room) water as follows:

20 mg/mL	0.20 g
40 mg/mL	0.40 g
60 mg/mL	0.60 g
80 mg/mL	0.80 g
100 mg/mL	1.00 g

   Bring to volume with MPA and store the individual standards in screw-cap vials.

3. Control Check: The control check is prepared from a 25% stock solution kept in the refrigerator. Prepare a 1:10 dilution of this as you would a sample, 1 mL in 10 mL volumetric with MPA and store in a screw cap vial. (The water and acetone were weighed out in the preparation of the stock, so the concentration is already g/mL, therefore all that is needed is to dilute 1mL to 10 mL.)

4. Samples: Prepare the samples as described in the sample preparation section. All samples and the Trip sample are prepared as 1:10 dilutions in MPA. The same dilutions are used for the Karl Fischer analysis and the acetone/alcohol analysis . Record the weights in the lab notebook.

5. Using a disposable pasteur pipet, transfer some of the MPA blank, standards, check, trip, and samples into appropriately labelled gc vials and crimp the caps on.

6. Check that there is sufficient He (the carrier gas) for the run. The tank should be changed when the pressure regulator is at 500 psi.

7. The GC conditions and settings are as follows:

Column:	Hayesep C 80/100 mesh 6ft x 1/8th in. od stainless steel packed column
Oven Temperature:	80°
Init Time:	1.20 min
Rate:	20.0°
Final:	210°
Final Time:	6.20 min
Injector Temperature:	250°
Detector Temperature:	250°
Det A TCD ON [+]	
TCD A: LOW SENS	
EPP A:	28.3 psi at 80°

8. Check to see which method is in the system. If the water method is already in, the oven temperature should be reading 80^0. If this is the case, Press DET A ON, this will turn on the TCD for the analysis. If the water method is not in, then in the HP CHEM station click on:

    ----METHOD Load, WATER

    It will take a few seconds for the program to load. The WATER method should now be available.

9. The GC should be ready to go, temperatures ready, detector on. Now need to load the sequence to set up the sample table to run on the autosampler. Click on:

    -----SEQUENCE
        Load, WATER

    The sequence is always WATER, the data files will be saved by date to identify them individually.

10. To identify the file, click on:

    ----Edit Sequence Parameter.

    Enter in the subdirectory a path for the data: Yr/Mon/Day, Eg. 961015A
    Press OK, this creates the subdirectory, under the WATER sequence
    If there is another with the same identification, use A or B, etc.

11. Now still in the Sequence table, click on:

    ------Edit Sequence Table
    Injector, FRONT

    Enter, Blank, the 5 standards, the blank again, the check, the trip, and the samples, the method is WATER and vial number on the tray.

    Each vial will have its own vial number, but the sequence number is just the line item number in the table. To run the blank and the check multiple times, just insert the vial number, it is not necessary to prepare a separate vial.

12. Now enter the individual samples, click on:

    ------Edit Sample Table

    Enter all samples, eg 9600080, and the vial number

13. Check to be certain everything has been entered correctly. Press SAVE in the Water sequence. Click on Print Sample Log Table. This will print out the sequence, double check that everything was entered correctly.

14. Click on :

    ------RUN CONTROL
    -----Run Sequence

15. After the sequence is complete, check the controls and see that they are all within the limits. Fill out the control check on the chart and in the lab notebook. Also indicate if there is anything detected in the blank. Print out the calibration curve for the standards.

16. Go over the chromatograms, check the MPA peak to be certain it is approximately the same height throughout the analysis. If a sample was misinjected, the problem will most likely show up in the MPA peak.

17. Check the chromatograms off and initial as you go over them, from the weights made from the dilutions mark on the print out the actual value for the sample.

18. Check that the Trip sample is correct.

19. Note any problems in the lab notebook.

20. Place the chromatograms and the calibration print out in a folder, label the sample numbers and file in the designated box.

GC Analysis Water

Date Analyst's Initials

Sequence Print Out

Blank
Calibration Standards
Blank
Check and again every 10th analysis
Trip
Samples
Final Check

(Example;

Seq#	Vial #	Description
1	1	Blank
2-6	2-6	Standards 1-5
7	1	Blank
8	7	Check
9	8	Trip
10-17	9-16	Samples
18	7	Check
19-27	17-25	Samples
28	7	Check

Blank: X.XX%
Checks: XX.XX/ XX.XX/ XX.XX%
Trip: XX.XX%

SOP REVISION HISTORY

1. May 16, 1996: Addition of trip samples to QC.

2. March 10, 1998. Adjusted document font to Times New Roman 12. Inserted appendix B formerly a stand-alone document.